

PMMA Development Studies Using Various Synchrotron Sources and Exposure Conditions

[§] Ming X. Tan, Michelle A. Bankert, Stewart K. Griffiths,
Aili Ting, Dale R. Boehme, Shondelle Wilson and Lianna M. Balser

Materials Processing Department, MS 9405, Sandia National Laboratories California, PO Box 969, Livermore, CA 94551

ABSTRACT

PMMA has been the primary resist used in synchrotron exposures for micro-machined parts fabricated by the LIGA process. Because development of this resist directly influences both tolerances and surface finish of completed LIGA structures, it is important to have a good quantitative understanding of PMMA development as a function of the absorbed dose, as well as both the exposure and development conditions. The various synchrotron sources used for LIGA fabrication vary widely in beam energy and flux, and these variations would be expected to influence development rates. Here we present a simple method to measure PMMA development rate over a moderate range of doses using only a single exposure at the synchrotron source. By employing several exposures, this method allows ready determination of development rates over a wide range of exposure and development conditions. Results are presented for the kinetics of PMMA development over a range of development temperatures, absorbed doses, dose rates and sample ages for exposures performed at three major x-ray sources in the United States

Keywords: LIGA, PMMA, development rate, synchrotron

1. INTRODUCTION

LIGA (the German acronym for lithography, electrodeposition and molding) is a relatively new method for fabricating precision, high aspect-ratio, micro-machined parts.¹⁻³ This process uses synchrotron radiation to expose a masked x-ray resist ranging in thickness from 50 nm to greater than 1 mm. Exposed regions are developed in an organic solution, and the cavities are then filled with metal by means of electrodeposition. The resulting metal structures can be used as an end product or may serve as a mold for the final molding operation. The LIGA process can produce finished parts having micron to millimeter sized features, very high aspect ratios, and side-wall slopes of less than 0.1 mm/mm.⁴

Poly-methylmethacrylate (PMMA) is the most commonly used resist in the LIGA field. The resist is first attached to a conductive substrate either by a polymerization casting method (involving the mixing of a low molecular weight PMMA with radical initiators and other additives),^{5,6} or by solvent bonding of free standing PMMA sheets (a thin film of PMMA is spin coated onto the conductive substrate, and the free standing sheet is bonded onto this film).⁷ During x-ray exposure, chain-scission reactions reduce the molecular weight of the PMMA in the regions of the sheet not masked. A developer solution is then used to selectively dissolve this low molecular-weight material. This dissolution or development rate is a function of the polymer molecular weight, which is related to the initial PMMA molecular weight, exposure dose, and the main-chain scission yield.⁸⁻¹⁰

Past research of PMMA development rate has focused largely on cast PMMA. These resists typically have a bimolecular weight distribution with mass-averaged molecular weights (MW) near 90,000 and 300,000 g/mol, and weight distributions ranging from $\gg 50,000$ to 10^7 g/mol.⁶ In contrast, current practice in the US LIGA community is to employ commercial free-standing PMMA sheets having a thickness from about 1 to 2 mm.¹¹⁻¹⁴ These sheets are usually fabricated through standard industrial monomer casting methods and typically have molecular weights greater than one million with no cross-linking. For example, the Perspex CQ samples used in the present study had a MW of 2.75×10^6 and distributions ranging from 600,000 to 13×10^6 g/mol. These PMMA samples should therefore not have the same development rate/dose characteristics as cast PMMA. Further, PMMA properties such as additives, degree of cross-linking, and annealing procedures can all lead to variations in the development rate for a given absorbed dose.

The purpose of our study was to measure development rates on these commercial PMMA sheets and to investigate the influences of the synchrotron source, absorbed dose, post-exposure sample age, development temperature and other factors

[§]Further author information:

M. X. T. (correspondence): Email:mtan@sandia.gov; Telephone 925-294-3643
Sandia LIGA Web Page: <http://daytona.ca.sandia.gov/LIGA/>

influencing these development rates. Because of limited synchrotron beam time available to LIGA users at the various synchrotron sources, it was necessary to minimize exposure times to the extent possible, while at the same time collecting a sufficiently large set of development rate data to yield statistically significant results. To this end, we utilized the depth dependence of the local absorbed dose to obtain a range of doses from a single exposure. By using the method described below, we were able to carry out a detailed study of PMMA development rates through minimum number of synchrotron exposures.

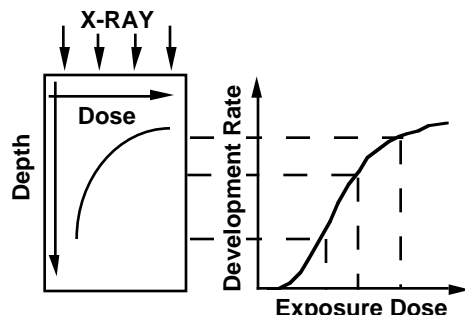


Figure 1. PMMA development rate/dose relationship as a function of depth.

As PMMA absorbs x-ray energy through a thick sample, there is a rapid decay of the local dose with increasing distance from the surface. By calculating the dose profile as a function of PMMA depth and measuring the development rate at various depths, development rate as a function of dose can be obtained with a single exposure (Fig. 1).

Using this method, we have obtained development rates at three major Department of Energy beam lines – the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford University, and the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory. We will report here the first order dependence of development rate on the absorbed dose at these three x-ray sources. Development rates as functions of other process parameters, such as developer temperature,

sample annealing schedule and post exposure sample age, are also reported. Although feature size can have profound effects on the development rate due to the transport of PMMA fragments from the dissolution surface,^{15,16} we will investigate here only the kinetics of development. Using these kinetics results, along with simple models of PMMA fragment transport, we will be able to optimize exposure doses and predict required development times for PMMA LIGA resists.¹⁷ Such quantitative results can also be used to optimize absorber thickness for LIGA masks.

2. EXPERIMENT

All PMMA samples used in our experiments were Perspex CQ 1 mm thick samples, obtained from the Goodfellow Corporation. The molecular weight distribution obtained from Gel Permeation Chromatography (GPC) measurements in tetrahydrofuran (THF) solutions by American Polymer Standards Corporation was: 2.75×10^6 g/mol for weight averaged molecular weight, with less than 5% below 0.6×10^6 or above 13×10^6 g/mol.

Exposures were carried out at three synchrotron sources – beam line X27B at NSLS, beam line 2-2 at SSRL, and beam line 10-32 at ALS. At SSRL and ALS, we used a scanner provided by the Jet Propulsion Laboratory. At NSLS, we used a scanner provided by Christopher Milne and Erik Johnson of Brookhaven National Laboratory. A 4 mm thick stainless steel plate with arrays of 6 mm diameter holes was used as the exposure mask. PMMA samples were stacked directly behind the plate. In order to obtain PMMA samples with various doses while carrying out a minimum number of exposures at the synchrotron source, aluminum foil pieces of thickness from 25 to 150 nm were used as filters between the stacked PMMA sheets or in front of the stainless steel mask. The specific stack sequences of the samples and filters for various experiments are listed in the results section.

All chemicals for the development experiment were obtained from Aldrich Chemical Company, Inc. In order to obtain maximum contrast and minimum solvent swelling induced stress problems, a very mild developer consisting of 60% 2-(2-butoxyethoxy)ethanol, 20% morpholine, 5% ethanolamine and 15% 18 MW de-ionized water was used. This mixture of solvents is commonly known as GG developer.^{6,10,18,19}

All development experiments were performed in developer solutions that were less than three days old. The development experiments were carried out in a beaker of stirred solution in air. On average, the stir speed was 500 RPM. We regulated the developer temperature at 35 ± 0.5 °C with a Brinkmann circulator bath. The back of the PMMA samples were each sealed with Kapton tape, so only the front faces of the samples were developed. A micrometer with accuracy of ± 2 μm was used to measure the thickness of each sample before and after taping. The samples were then immersed in the developer. At time intervals ranging from 5 to 30 minutes, the samples were taken out of the developer, rinsed with de-ionized water, air dried, and the remaining thickness of the exposed PMMA was measured. We then re-immersed the samples in the developer bath, and the process was repeated until the exposed PMMA was completely developed, or until the thickness change was less than 2 μm over a period of one hour. Total development time varied from 2 hours to over 24 hours. In all experiments, the volume of the bath was 1 liter, and the amount of PMMA dissolved was less than 0.8 grams. This change in concentration of <1 g/L should not significantly influence the development rates.

The PMMA doses absorbed at various depths within the sample were calculated using the Sandia developed computer code known as LEX. Comparisons between the output of LEX and other software such as CXRL ToolSet²⁰ and Photon²¹ showed that all three codes provide very similar results.

3. RESULTS AND DISCUSSION

The PMMA exposures performed in this study use three different beam lines (NSLS, SSRL and ALS) having different beam energies and flux outputs. NSLS operates at 2.6 GeV with a maximum beam current of 300 mA; SSRL has an energy of 3.0 GeV but a maximum current of only 100 mA; while ALS runs in both 1.9 GeV and 1.5 GeV modes, with currents of 200 mA and 400 mA respectively. These differences in energy and flux have a significant influence on dose rates and dose profiles through the PMMA thickness.

In a typical run at NSLS we exposed three layers of PMMA with top doses of 4.7, 2.8 and 1.9 kJ/cm³. Each layer contained four identical circles of PMMA that received the same exposure. Each of these circles was then developed to obtain the measurements of development depth (δ) versus time (t) shown in Figure 2a. The development rate (μ) corresponding to each depth (δ_i) was then calculated by direct numerical differentiation.

$$\mu_1 = \frac{\Delta\delta}{\Delta t} = \frac{\delta_1 - \delta_2}{t_1 - t_2} \quad (1)$$

The resulting development rates shown in Figure 2b are somewhat noisy, as expected in differentiating data. But the induced scatter of about 30% is not much greater than the differences between the four data sets obtained under nearly identical conditions.

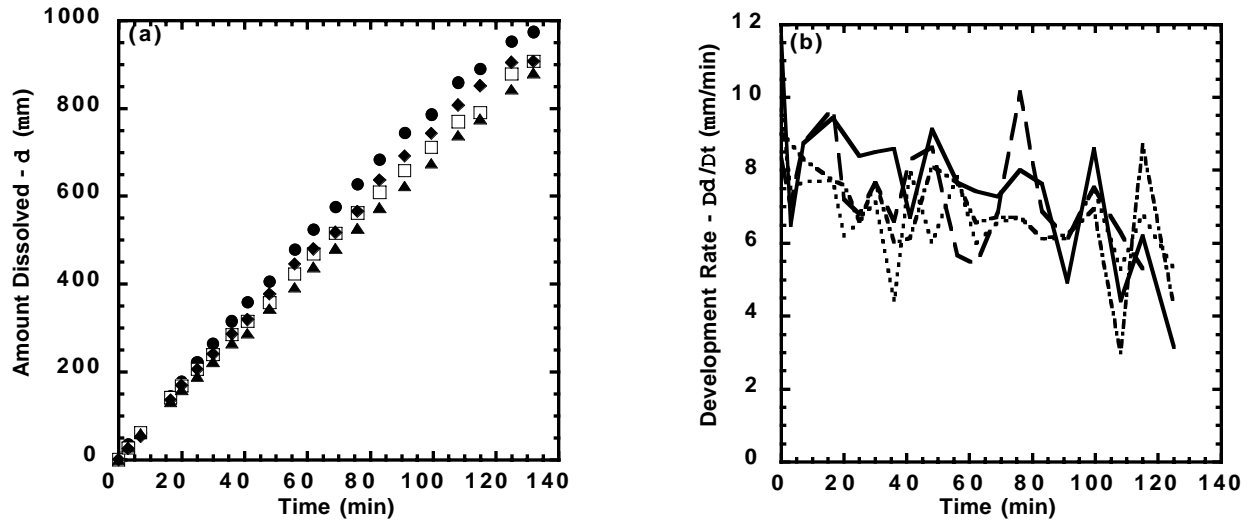


Figure 2. Development results for four PMMA circles with a top dose of 4.7 kJ/cm³ (exposed at NSLS) in a 35 °C developer. (a) Amount of PMMA dissolved as a function of time for four circles with identical dose. All four circles were developed at the same time to get a better estimate of the experimental measurement errors. (b) Development rate as a function of time.

The next step of our data analysis is to relate these measurements of development rate to the absorbed dose (D) at each depth (δ) within the PMMA sample. The doses were calculated using the LEX code, as mentioned earlier. Figure 3 shows a plot of development rate versus dose for the data of Figure 2. The shape of these curves suggest that they can be fit with a function of the following general form,

$$\mu = \frac{aD^\alpha}{1 + bD^\alpha} \quad (2)$$

where a , b and α are adjustable parameters. This function is chosen because it replicates the well-known power-law dependence of development rate on dose at low doses, but also permits the development rate to reach a plateau value as the dose becomes very large and the PMMA molecular weight approaches its limiting value. This limit is the result of a

combination between chain scission reactions on the polymer back bone and the cross-linking reactions of the short PMMA chains.^{9,10}

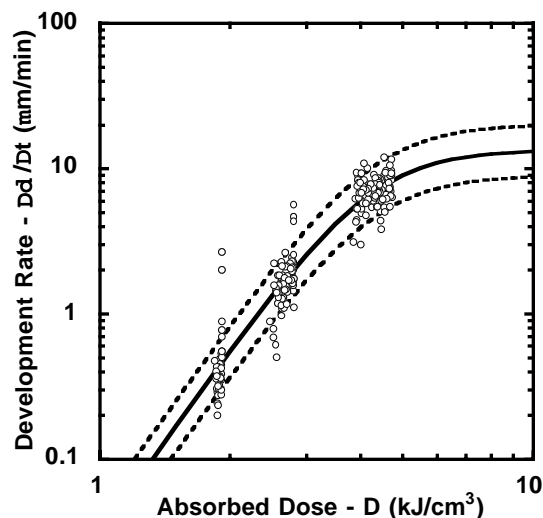


Figure 3. Development rates for NSLS exposure. The exposure time was about three hours and scan length was 7.4 cm. All samples were exposed from this single exposure. The filters used were 500 mm Be, 50mm Al, 200mm Si, and with an 80 cm air path. The first layer of PMMA received a top dose of 4.7 kJ/cm³. A 90 mm Al filter was used between this layer and the second layer of PMMA, which had a top dose of 2.8 cm³. This was followed with 85 mm Al and the third layer of PMMA with a top dose of 1.9 kJ/cm³. The symbols represent the development rates obtained from all the PMMA samples. The solid line represents the least-squares fit to the data. The dashed lines represent a relative error range of ~50%.

Although the data shown in Figure 3 do not quite reach the expected development-rate plateau, this feature can be seen in later results from SSRL and ALS exposures. We also plan to perform NSLS exposures at doses higher than our current maximum level of 5 kJ/cm³ to verify the level of the plateau shown above.

The majority of data in Figure 3 lie within the dashed lines indicating ~50% relative deviations from the fit. This scatter is mainly due to inaccuracy in measuring development depths and calculating development rates, as earlier apparent in Figure 2b. There are certainly many reasons to expect such deviations, given the multistep process of removing samples from the developer solution, rinsing them off, measuring the sample thickness with a micrometer, and returning them to the bath. For this reason, we chose to measure time only to the accuracy of ~1 minute, roughly the amount of time taken to remove a sample from the bath and completely rinse off the developer. These sources of error in measuring the development time are certainly much greater than those associated with measuring the sample thickness with a micrometer, so there is little reason for using a more accurate surface profilometer. Much more could be gained by devising a method to measure PMMA thickness during development, without removal from the bath. Unfortunately, standard interferometric thickness monitors are not suitable for this application because of the large PMMA thickness. Moreover, our present approach provides the needed information, with reasonable accuracy, and with moderate expenditures of exposure and development time.

Since our intent is to measure chemical reaction kinetics, every effort is made to avoid diffusion limitations on development rates. Our exposed circles have a diameter of 6 mm, more than six times greater than the sample thickness. This low aspect-ratio geometry coupled with vigorous stirring of the bath ensures that the developer concentration at the PMMA surface is nearly the same as that in the bulk solution. Under these conditions, diffusion effects are minimal, and the development rate reflects only the reaction kinetics of the development process. Smaller features with higher aspect ratios will develop much slower than these circles. However, the development rate in these smaller LIGA-like features can be predicted by combining the present results with modeling of diffusive and convective transport within features. Such calculations of development rates in high aspect-ratio features will be presented and compared with experimental observations in a separate paper.

Figure 4 shows the relationship between development rate and absorbed dose for samples exposed at SSRL. It is important to notice that development rates, obtained from the two samples with top doses of 6.3 kJ/cm³ and 4.3 kJ/cm³ respectively (regions II and IV on the figure), overlap well with the samples with top doses of 8.4 and 5.4 kJ/cm³ but with bottom doses of 6 and 4 kJ/cm³ (regions I and III). This indicates that within our experimental error, a development rate obtained from a specific depth (d_1) in a thick sheet at dose $D(d_1)$ agrees with the rate in another sheet with a top dose value also of $D(d=0)$. This consistency in the data also indicates that there is no significant preconditioning of the PMMA, such as solvent swelling, occurring prior to the arrival of the dissolution front. Thus, it appears that development rates are controlled only by the absorbed x-ray dose. This is the basic premise of our approach to constructing development rate profiles from exposure of a single sample. Similar fits to the development rates for exposures at ALS are shown in Figure 5.

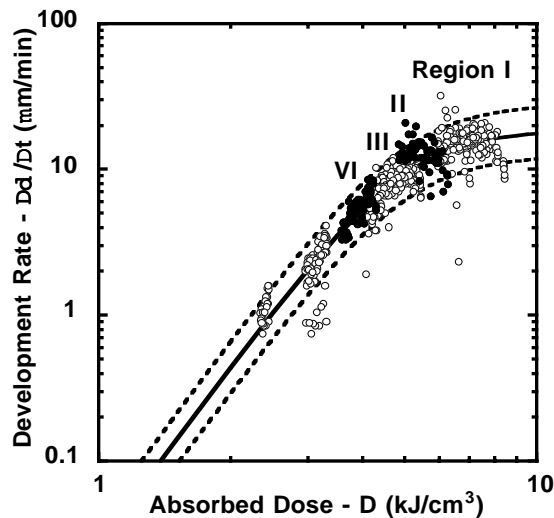


Figure 4. Development rates for SSRL exposure. Six different surface doses were obtained with a single exposure of about 20 hours. The filters used were 533 mm Be, 10 m He, 15 mm C, 35 mm Al and 15 cm of air path. The first layer of PMMA had 12 exposed circles, nine of them were covered with 110 mm Al on top to achieve a dose of 8.4 kJ/cm^3 (), and three of them had 150 mm Al on top to achieve a top dose of 6.3 kJ/cm^3 (•); the second layer of PMMA was placed behind the first layer with no Al in between and had doses of 5.5 () and 4.3 kJ/cm^3 (•); the last layer of PMMA had 29 mm Al covering 9 circles, 58 mm Al on the other three circles, and the exposed top doses were 3.7 and 2.9 kJ/cm^3 respectively (). Again the solid and dashed curves represent the least-squares fit and $\pm 50\%$ relative error bands.

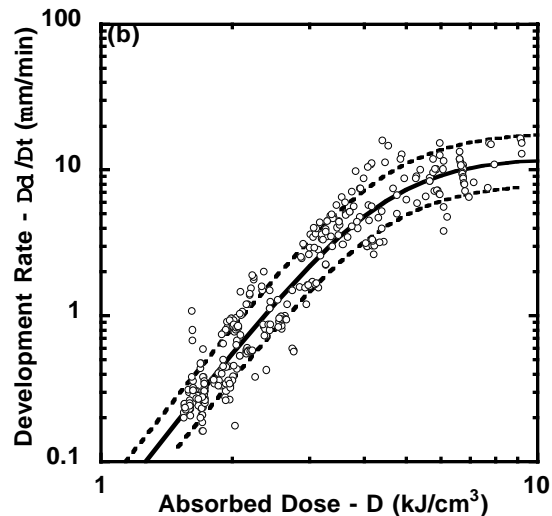
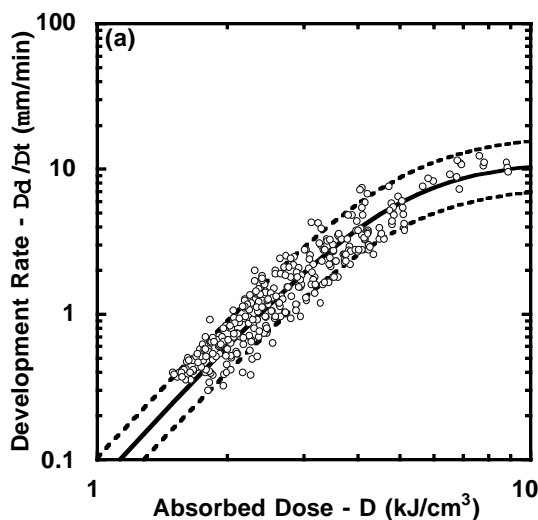


Figure 5. Development rates obtained for ALS exposure, beam line 10-32. (a) Development rates from seven different top exposure levels when ALS was operating at 1.5 GeV. The filters used were: 127 mm Be, and 45 mm Al, followed by 1.4 cm to 2 cm of air. Exposure time varied from 18 hours to 35 hours. Only a few samples with very low doses of $2\text{-}3 \text{ kJ/cm}^3$ were exposed as second layer PMMA. All other samples were exposed as first layer. (b) Development rates from six samples when ALS was operating at 1.9 GeV. 127 mm Be, 35 mm Al and 2 cm of air path was used during exposure ($>5\text{-}7$ hours). Similar to samples from 1.5 GeV exposure, only a few samples with very low doses were second layer PMMA.

A comparison of development rates for exposures at the three sources and two beam energies of ALS is shown in Figure 6. The development rates are similar for samples exposed at SSRL (3.0 GeV) and NSLS (2.9 GeV). Those exposed at ALS (1.9 GeV) are somewhat lower, and those exposed at ALS (1.5 GeV) showed the lowest development rates of all. This suggests that development rate is not only a function of the absorbed dose but also is effected by beam energy and/or the incident flux. However, variations in dose rate between the three sources do not seem to contribute to the beam line dependence observed here. The exposure times of greater than 20 hours for samples from ALS (1.5 GeV) and SSRL were much longer than the exposure times at NSLS (3 hours) and ALS 1.9 GeV (>6 hours). As such, dose rate alone does not appear capable of explaining these differences. Moreover, because any PMMA heating during exposure should be proportional to the dose rate, differential heating between the three sources also cannot explain these discrepancies in development rates. Based on these observations, we tentatively conclude that the differing development rates result from small differences in the scission yields for the differing x-ray photon energies produced by the three machines.

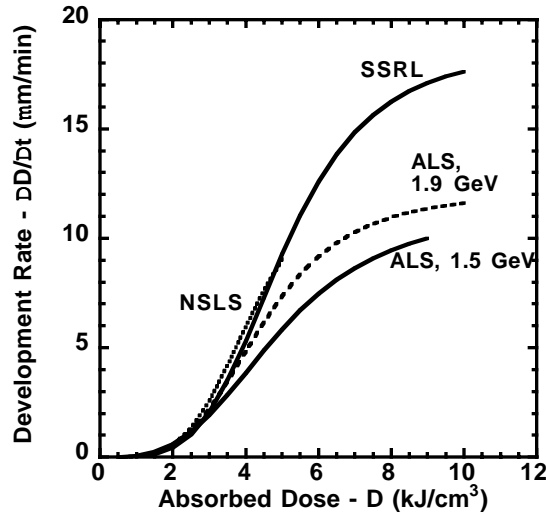


Figure 6. Development rates for PMMA samples exposed at ALS, NSLS and SSRL.

The development rates obtained here are all lower than the development rates of cast linear polymers reported by Mohr *et. al.*⁶ For example, at an exposure dose of 6 kJ/cm³, a PMMA development rate of almost 30 mm/minute was reported. We believe the slower development rate here is due to the high initial PMMA molecular weight of our commercial resists. Studies of similar types of PMMA at slightly lower developer temperatures (30 °C) from exposures at the Advanced Photon Source at Argonne National Laboratory reported a development rate of about 13 mm/minute for a dose of 6 kJ/cm³, which agrees with our results from SSRL.¹⁴

From this plot, we suggest an optimum exposure dose of 6 to 8 kJ/cm³ for normal LIGA exposure conditions. Higher doses are not recommended because they do not increase the development rate significantly and may lead to physical damage of the PMMA. Lower doses are also not recommended due to slow development rates. In fact, for doses below 2 kJ/cm³, development rates fall below 1 mm/minute, which often extend development time beyond 24 hours for a 1 mm thick LIGA part. Such long development times tend to result in PMMA swelling and the accompanying loss of tolerances in very fine LIGA features.

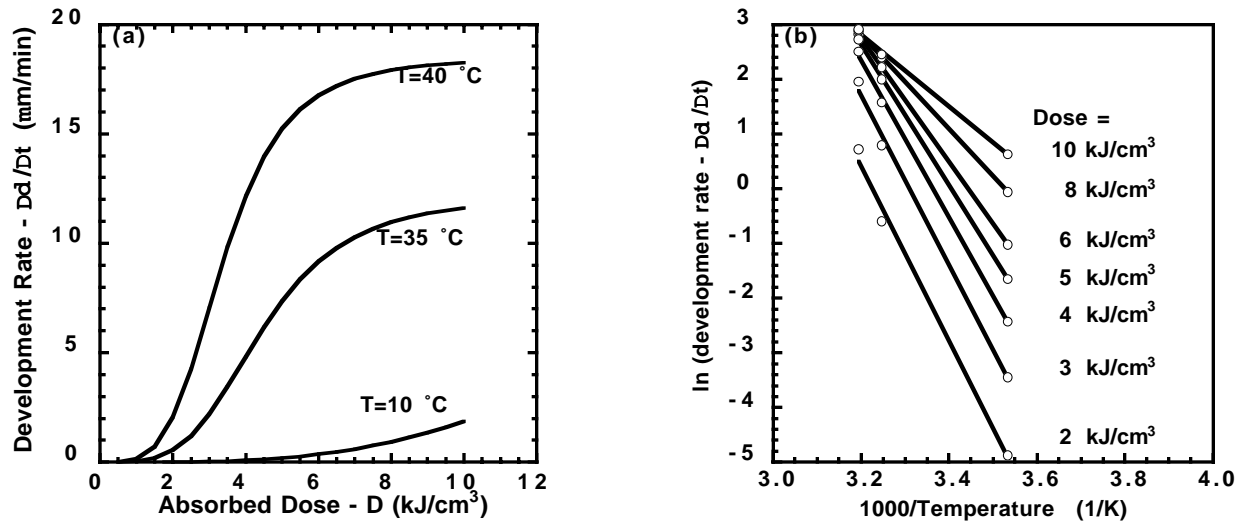


Figure 7. Development rates of PMMA samples as a function of developer temperature. The exposure conditions for these samples were the same as those exposed at ALS under 1.9 GeV operation conditions (Fig. 5).

To investigate the temperature dependence of development rates, we developed some of the samples obtained from exposure at ALS (1.9 GeV) at different developer temperatures. As shown in Figure 7a, development rate changes drastically

with temperature. The activation energy, E_a , for the development process is related to the development rate (μ) by the relations

$$\mu = C \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

$$\ln(\mu) = \ln(C) - \frac{E_a}{RT} \quad (4)$$

where T is the absolute temperature of the developer and C is a constant. From Figure 7b, we calculated the activation energy as being in the range of 55 kJ/mol at a 10 kJ/cm³ dose to 130 kJ/mol at a 2 kJ/cm³ dose. The activation energy decreases smoothly with increased dose. This dose dependence agrees with the study of cast PMMA development by Stulz,²² and is similar to other reports of activation energies for PMMA development.²³

As part of this study, we also examined the effects of PMMA annealing schedules and the post-exposure sample age on the development rate. In previous work, we have noticed that annealing the PMMA samples prior to the exposure is beneficial in preventing cracks in developed LIGA parts. To examine the influence of this heat treatment on development rates, we have compared the rates of three samples exposed at SSRL. One sample was annealed for 2 hours at 120 °C followed by a 1 °C/minute cooling rate, one was annealed for 6 hours at 100 °C, and the other was not annealed. Within our experimental error, we did not observe any changes on the development rate. While there have been reports of PMMA chain scission yields increasing upon annealing at about 150 °C,²⁴ such effects must be secondary and cannot be confirmed by our current results.

We also had observed that the spreading of cracks and PMMA discoloration in the exposed regions increase with time after exposure. Despite these observations, we did not detect any differences in the development rates of three samples exposed at NSLS and developed one week, three weeks, and six months after exposure.

4. SUMMARY

We have undertaken a broad experimental program examining several of the many factors influencing development rates of sheet PMMA used as an x-ray resist in the LIGA manufacturing process. The factors investigated here include beam energy of the x-ray source, absorbed dose, dose rate, post-exposure sample age, development temperature, and annealing schedule. Exposures were performed using three different sources, NSLS at Brookhaven, SSRL at Stanford, and ALS at Lawrence Berkeley Laboratory. These three sources all have different beam energies and flux outputs. NSLS operates at 2.6 GeV with a maximum beam current of 300 mA; SSRL runs at 3.0 GeV with 100 mA maximum beam current; and ALS runs at both 1.9 GeV and 1.5 GeV mode, with currents of 200 mA and 400 mA respectively.

Of the factors studied here, development temperature clearly has the strongest influence on development rate. Based on exposures performed at ALS only and development temperatures ranging from 10 to 40 °C, observed activation energies for development of commercial PMMA sheet varied between about 130 and 55 kJ/mol for absorbed doses between 2 and 10 kJ/cm³. The activation energy is highest at the lowest doses and decreased smoothly with increasing dose. The magnitudes of these values and the trend of decreasing activation energy with increasing dose are consistent the observations made in previous studies.^{22,23}

The nature of the x-ray source affected development rates. Although this influence is much weaker than that of the development temperature, our results showed a clear and non-negligible reduction in development rates at a given dose with increasing beam energy. NSLS and SSRL, both near 3.0 GeV, yielded the highest rates and rates very similar to one another. ALS at 1.9 GeV yielded somewhat lower development rates, and ALS at 1.5 GeV produced the lowest. The differences in development rates were most pronounced at the higher doses, suggesting that cross-linking reactions as the PMMA molecular weight approaches its limiting value may play a role in the differences. In any case, the overall scission yields for the three machines were very similar, though apparently somewhat higher for higher beam energies. These differences between development rates for the three machines cannot be attributed to an influence of dose rate. Although the beam lines used at SSRL and NSLS produce fluxes that differ by nearly a factor of three, development rates for exposures at these two sources did not differ significantly.

The remaining factors of annealing and post-exposure sample age showed little or no affect on development rates.

5. ACKNOWLEDGMENTS

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